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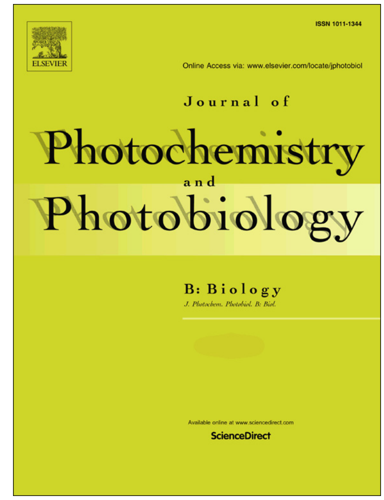

Organic Reactions for the Electrochemical and Photochemical Production of CO_2 to Fuels-The Reduction Chemistry of Carboxylic Acids as Bent CO_2 Surrogates, Aldehydes, Alcohols and Alkyls

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Organic Reactions for the Electrochemical and Photochemical Production of CO_2 to Fuels- The Reduction Chemistry of Carboxylic Acids as Bent CO_2 Surrogates, Aldehydes, Alcohols and Alkyls

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Abstract

The present review highlights the organic chemistry involved in the reduction of CO_2 and related intermediates to chemical fuels. We focus on known chemical reactions of CO_2 with organic molecules to yield carboxylic acid derivatives that create opportunities for reductive tandem electrochemical/chemical processes emerge. We draw parallels between long-standing knowledge of CO_2 reactivity from organic chemistry, organocatalysis, surface science, electrocatalysis and theoretical calculations related to these processes. We also point out some possible non-faradaic chemical reactions that could contribute to observed product distributions in the production of solar fuels from CO_2.

9.0. The Reduction of Alcohols to Alkyls

9.1. Barton-McCombie Deoxygenation

9.2. Electrochemical Deoxygenation

10.0 Conclusions

1. Introduction

Carbon dioxide (CO_2) is a linear molecule that has attracted attention in recent years a source of renewable energy through its conversion to chemical fuels[1]. The current discussion will highlight the use of molecular preactivators to alter the structure of the CO_2 molecule for selective access to high-value fuels *via* chemical and electrochemical means. We emphasize the chemical transformations of directly relevant functional groups and point out chemical reactions related to the observed chemistry.

In order to achieve the efficient conversion of CO_2 to chemical fuels, a catalyst is generally required to lower the activation energy of the chemical reduction, and many reaction pathways with comparable activation energies or shared reaction intermediates are generally accessible, leading to a variety of reaction products during catalysis. Although significant effort has been specifically centered on catalyst development for reducing CO_2 in solution, this overview aims to draw attention to examples of CO_2-bending reactions with organic bases to form carboxylate intermediates as starting points for reactions related to CO_2 conversions. Under this paradigm, the reduction of CO_2 becomes an exercise in the electrochemical reduction of carboxylic acids and derivatives, where a wealth of knowledge from organic chemistry comes into play.

The use of substoichiometric concentrations of certain organic molecules and their intrinsic reactivity as catalysts or mediators for chemical processes defines the field of organocatalysis [2, 3]. At the same time, these transformations are directly reminiscent of reactions in nature, where cofactors and coenzymes mediate biological pathways[4]. Such organic-mediated transformations with regards to the conversion of CO_2 to chemical fuels have been reviewed by Hu and coworkers[5]. The work summarizes the use of tetraalkylammonium salts[6], ionic liquids[7], and pyridinium derivatives[8] that have been successfully shown to act as mediators in the selective (photo-) electrochemical reduction of CO_2 to products such as CO and methanol.

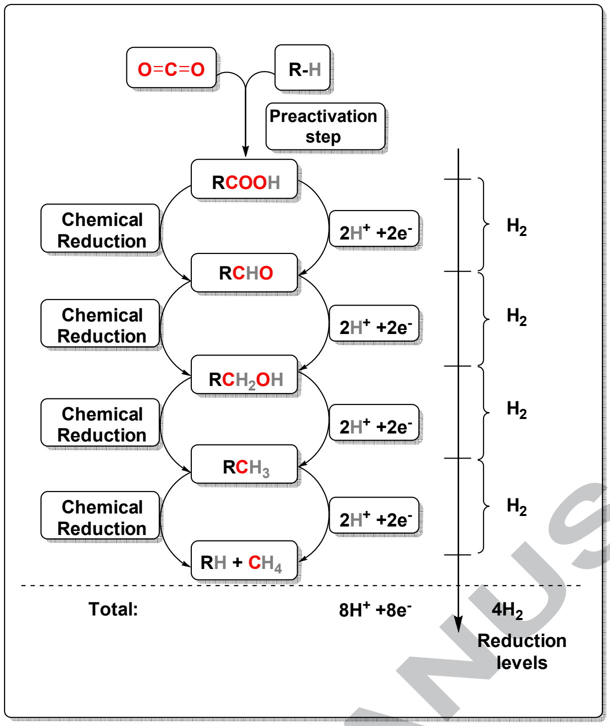


Figure 1. Opportunities for Tandem Chemical/ Electrochemical CO_2 reduction to fuels. [1]

We recognize that the organic reductive chemistry of carbonyl-containing moieties generally involves the formation of an activated adduct as a first step. Transformations of this kind, such as the Wolff-Kishner (Sections 8.1) and the related Caglioti reaction (Section 8.2) and as two examples, involve the formation of an activated intermediate poised to undergo further reduction.

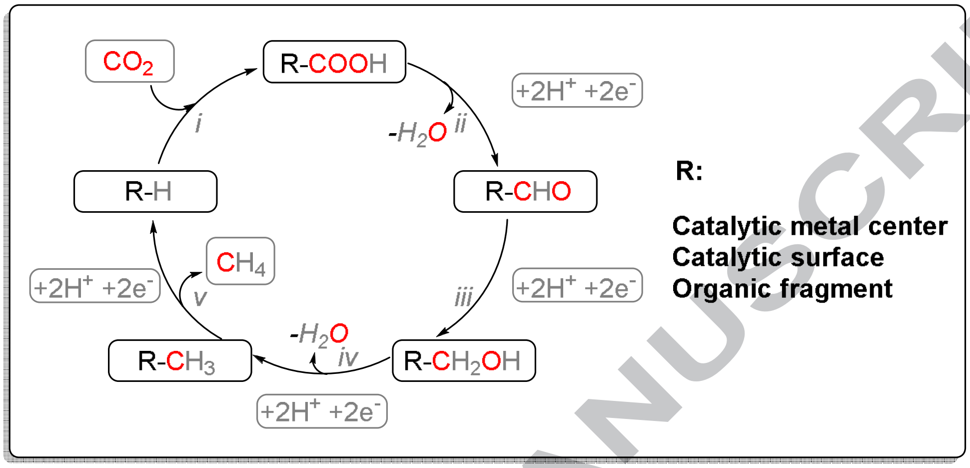
This particular strategy is an opportunity for new directions in the electrochemical reduction of CO_2 (Figure 1), where chemical transformations to form more easily reduced species could be performed in tandem with electrochemical transformations, when needed. Given this approach, to the best of our knowledge, reactions such as the Eschweiler-Clark (Section 8.5) and Crossed Cannizzaro (Section 7.2) have not ever been addressed as possible contributors to observed product distributions in current efforts in electrocatalysis for CO_2 conversion to fuels.

We limit the current discussion to organic-mediated, stoichiometric transformations and their mechanisms. Several of these reactions have been performed through transition-metal catalyzed hydrogenation and transfer hydrogenations. These reactivities remain outside the scope of the current discussion as they have been described elsewhere.[9-13]

2. CO_2 Reduction Chemistry and Intermediates in Solar Fuel Production

Organic molecules regenerated at electrode surfaces have been shown to perform energy-relevant redox chemical transformations [14] [3] [5]. Such molecules have also been involved in metal/ligand cooperativity in electrocatalytic dehydrogenation reactions with molecular precursors. No activity was observed in the absence of the redox-active component[15, 16].

Scheme 1 depicts a reduction pathway from a carboxylic acid down to an overall 8 H^+ and 8 e^- reduced species: CH_4. This particular scheme highlights opportunities for tandem conversion processes, catalytic or otherwise.



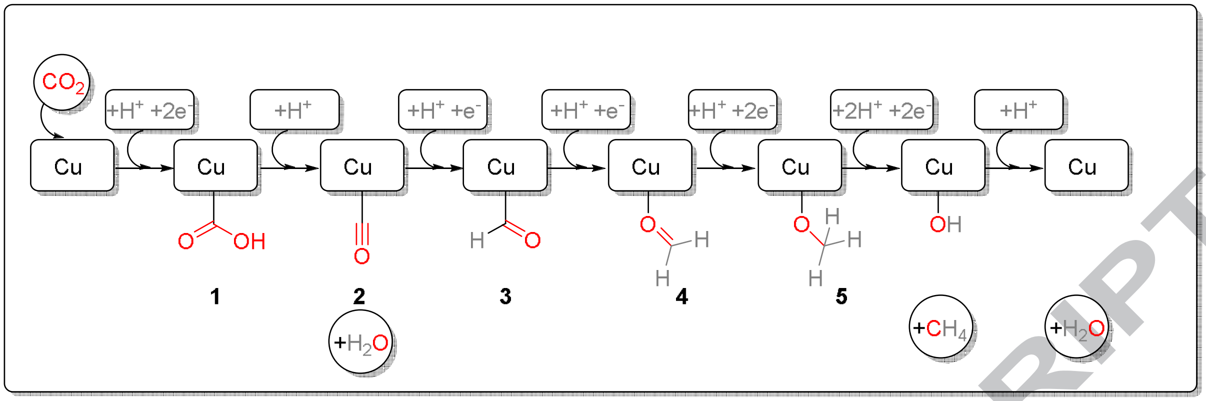
Scheme 1. General CO_2 reduction pathway *via* a Preactivation motif: *i* Prebending of the CO_2 prior to any chemical transformation.

During the preactivation step (*i*) the CO_2 molecule is converted to a carboxylic acid. A carboxylic acid (RCOOH) can then be converted to an aldehyde (RCHO) by 2 H^+ and 2 e^- (*ii*) which can subsequently be reduced to an alcohol (RCH_2OH) (*iii*) and then further to an alkyl (RCH_3) (*iv*) which could release the carbon fragment as CH_4 in a R-C bond-breaking event (*v*).

2.1. Intermediates in the CO_2 Electroreduction at Cu Surfaces

Heterogeneous electrocatalysis of the CO_2 reduction reaction comprises one of the largest technology gaps for efficient, sustainable CO_2 reduction and as such, the work discussed herein is a novel direction for the field and will likely enable the deployment of efficient, sustainable fuel generation. Homogeneous electrocatalysis has the advantage of tunability of the catalyst at the molecular level, however the operating conditions render current state-of-the-art systems technologically irrelevant[17]. Coupling the electrocatalytic reactions (both homogeneous and heterogeneous) with sorption and preconversion of CO_2 from the atmosphere will likely yield discoveries that translate from basic materials discovery, through cathode/catholyte components, to design of test-bed prototypes in the future.

In computational work by Nørskof [18] and coworkers, sequential reduction steps from CO_2 to methane are addressed as depicted in Scheme 2. Comparisons between enzymatic CO_2 reduction activities with heterogeneous metal surface [19] electrocatalysis bring forward a rate-determining step involving a CO-bound intermediate.



Scheme 2. Electrochemical Reduction of CO_2 to methane –theoretical calculations[18].

The mechanistic work proposes a series of chemical transformations as depicted in Scheme 1 and 2 with the formation of a carboxylate intermediate (**1**) as the first step in the process. In this particular regime, the carboxylate can then undergo a dehydration reaction to yield a bound [Cu-CO] (**2**) fragment, which then can be further reduced to a formyl fragment [Cu-CHO] (**3**) followed by an additional reduction to an O-bound formaldehyde species [Cu-OCH_2] (**4**) and then to a methanolic unit [Cu-OCH_3] (**5**) that can release CH_4 upon further reduction[18].

2.2. Catalytic Cycle with Molecular Preactivation – Intermediates and Functional-Group Interconversion Overview

Given the context of heterogeneous electrocatalysis in Section 2.1, our current discussion will focus on reductive functional group interconversions between carboxylic acids, aldehydes, alcohols and alkyls and we highlight examples of reactions involving both chemical and electrochemical regimes as can be seen in Figure 2. The related conversions and sections of this review are summarized in Table 1.

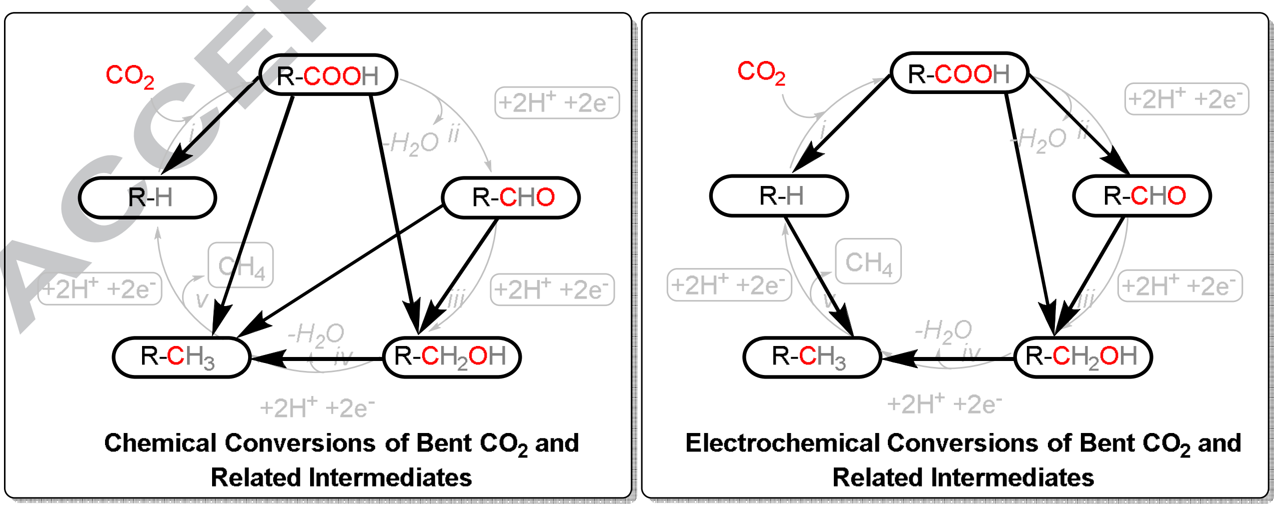


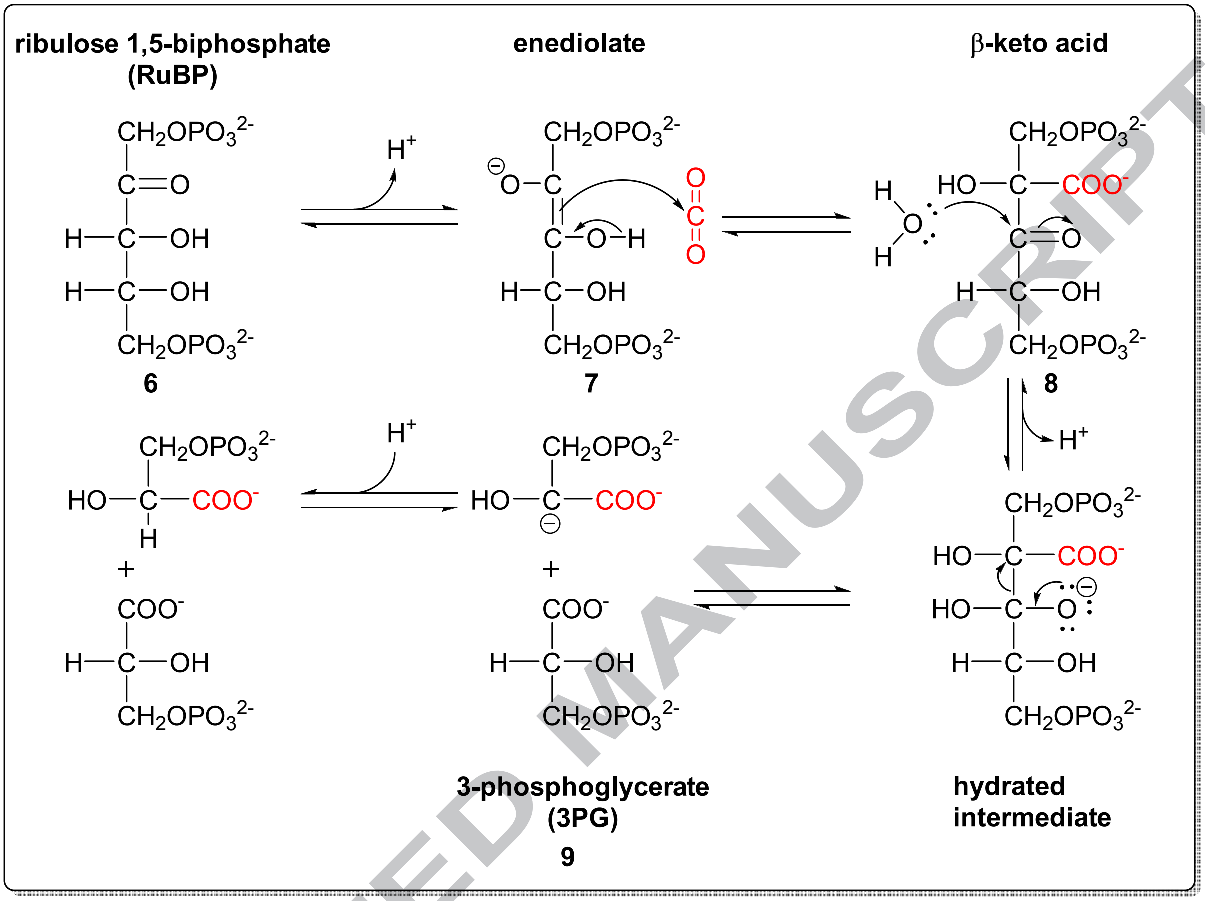
Figure 2. Chemical *vs* electrochemical conversions laid out in this review.

Table 1. Overview of reactivity discussed in the present work.

Starting Materials \ Products	RCOOH	RCHO	RCH_2OH	RCH_3	RH
RCOOH		Section 4	Section 5	Section 6	Section 6
RCHO			Section 7	Section 8	n/a
RCH_2OH				Section 9	n/a
RCH_3					n/a
RH					

3. Activation Chemistry of CO_2: Formation of Carboxylic Acids

3.1. Photosynthesis: RuBisCo and the Calvin Cycle



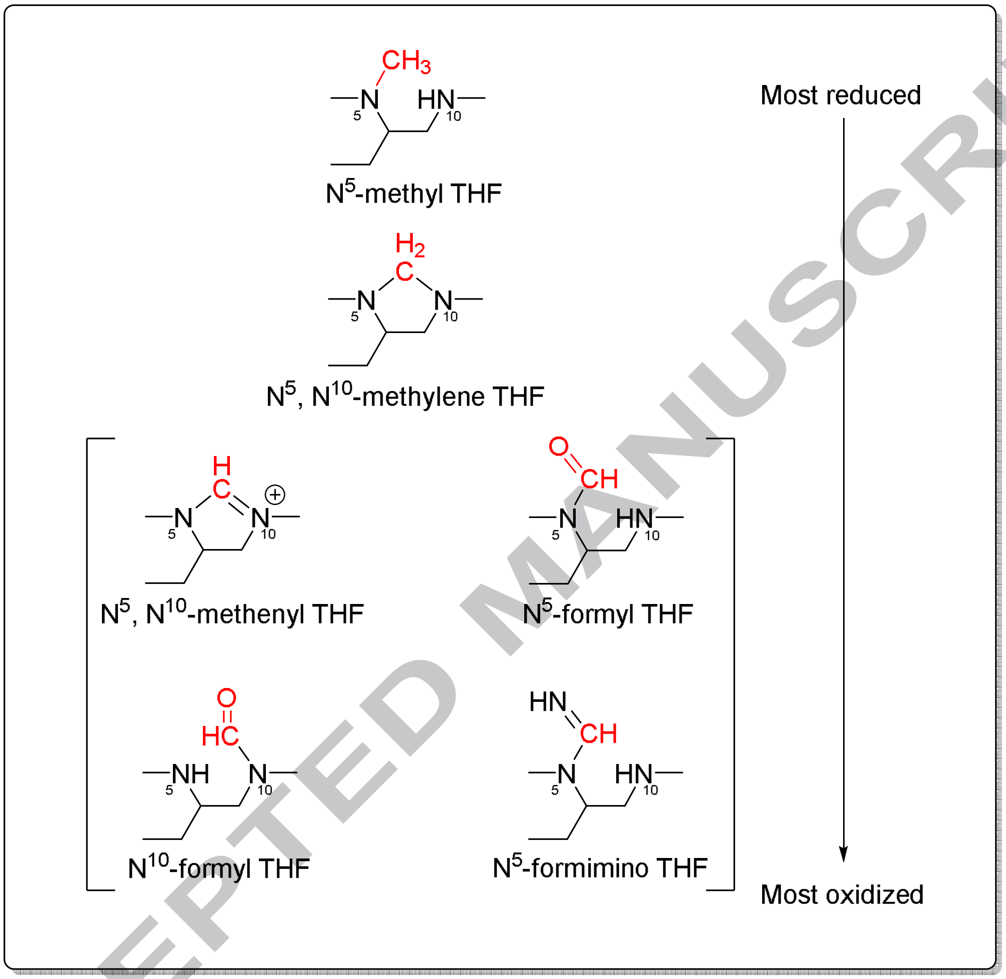
Scheme 3. CO_2 activation by ribulose 1,5-phosphate as the first step in Ribulose-1,5-bisphosphate carboxylase (RuBisCo) carbon fixation.

In process of natural photosynthesis, photosystem I is the membrane–bound unit where CO_2 is captured from the atmosphere and converted to sugars. The Calvin cycle is the metabolic pathway of CO_2 capture and conversion of sugars that takes place in the stroma of the chloroplast. RuBisCo – (Ribulose-1,5-BISphosphate Carboxylase/Oxygenase) is the enzyme responsible for the carbon fixation mechanism as described in Scheme 3. RuBisCo is believed to be the most abundant protein on Earth [20, 21].

The process occurs through a series of steps using ATP as an energy source and $NADPH_2$ as terminal reductant. The first step is the step of interest in the present discussion: carbon capture. The second and third phases of the cycle use the reducing equivalents from $NADPH_2$ and ATP to form sugars (step 2) and then regenerate RuBisCo in step 3. The net stoichiometry of the overall Calvin cycle suggests that for every three molecules of fixated CO_2, one molecule of 3-phosphoglycerate (3PG, **9**) is formed at the expenditure of nine molecules of ATP and six $NaDPH_2$.

As can been seen in the first step, the CO_2-trapping event occurs *via* a nucleophilic attack of an enediolate (**7**) onto CO_2 to yield a β–ketoacid (**8**). After a sequence of steps, the bound CO_2 gets converted to energy-rich molecules such as glucose.

3.2. C1-carriers in Nature: Folate Chemistry



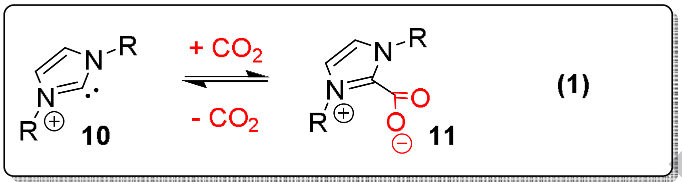
Scheme 4. Hydrofolate intermediates as C1 carriers in nature [22, 23].

Folates are N-containing chemical compounds responsible for aiding in the interconversion of formyl fragments to methyl in biological systems. They act as C1 carriers between several oxidation states of the carbon-containing organic fragment. The observed structures (Scheme 4) show several intermediates in folate metabolism including a range of N-bound methyl, formyl, methylene, methenyl and formimino fragments.

Such chemical transformations have been highlighted in reports related to tetrahydrofolate and tetrahydromethanopterin as different C1 carriers[22, 24]. The role of such conversions have been suggested in methanogenesis pathways[25-27]. Interestingly, a report on the involvement of such intermediates in the conversion of acetate into methane has also been made available[28].

3.3. CO_2 binding to Organic Bases in the Absence of an Added Stabilizing Lewis Acid

3.3.1. N-Heterocyclic carbene (NHC) Carboxylates



N-heterocyclic carbenes (NHC, **10**) have had a long-standing role in transition metal catalysis as versatile ligand frameworks with easily modulated donating properties[29]. The advent of organocatalysis has now exploited the organic fragments themselves as catalysts for a myriad of organic transformations in metal-free conversions[30, 31]. Most excitingly, the N-heterocyclic carbene fragments have been shown to react with CO_2 to form zwitterionic imidazolium carboxylates (Eq 1, **11**)[32]. These compounds were first reported as a protection method for air-sensitive NHC fragments and as precursors for NHC ligands for the synthesis of transition-metal complexes.

Louie and coworkers have now shown that the strength of binding CO_2 to the NHC fragment is tunable in a series of decarboxylation and transcarboxylation studies[33, 34]. Thermal stability studies have yielded a series of data shown in Figure 3[35, 36]. From the available data, we have observed a trend in the temperature (T) of CO_2 release of these zwitterionic species. The T correlates linearly with the dihedral angle between the CO_2 fragment (red) and the NHC fragment (blue) of these zwitterionic species. The zwitterions with the more electron-donating and less sterically-hindered NHCs **12** and **13** are almost flat, thus suggesting strong binding and possible conjugation with partial double-bond character between the CO_2 fragment and the NHC.

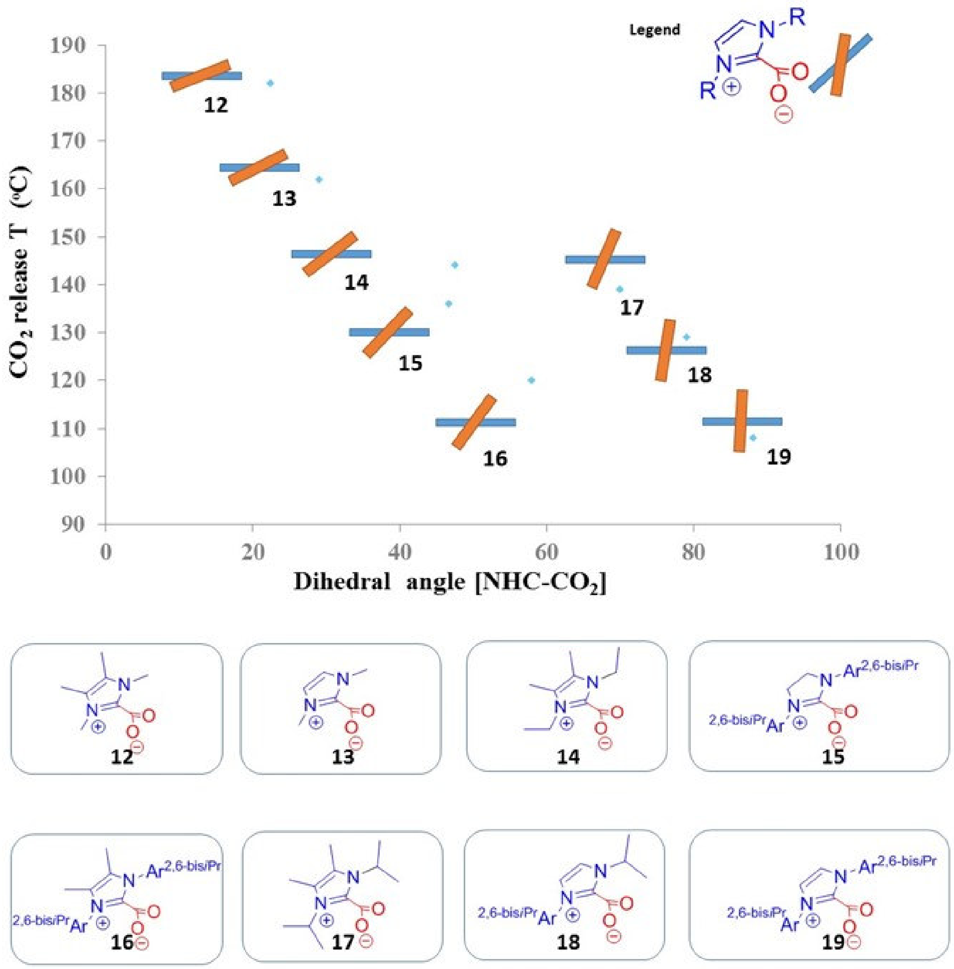
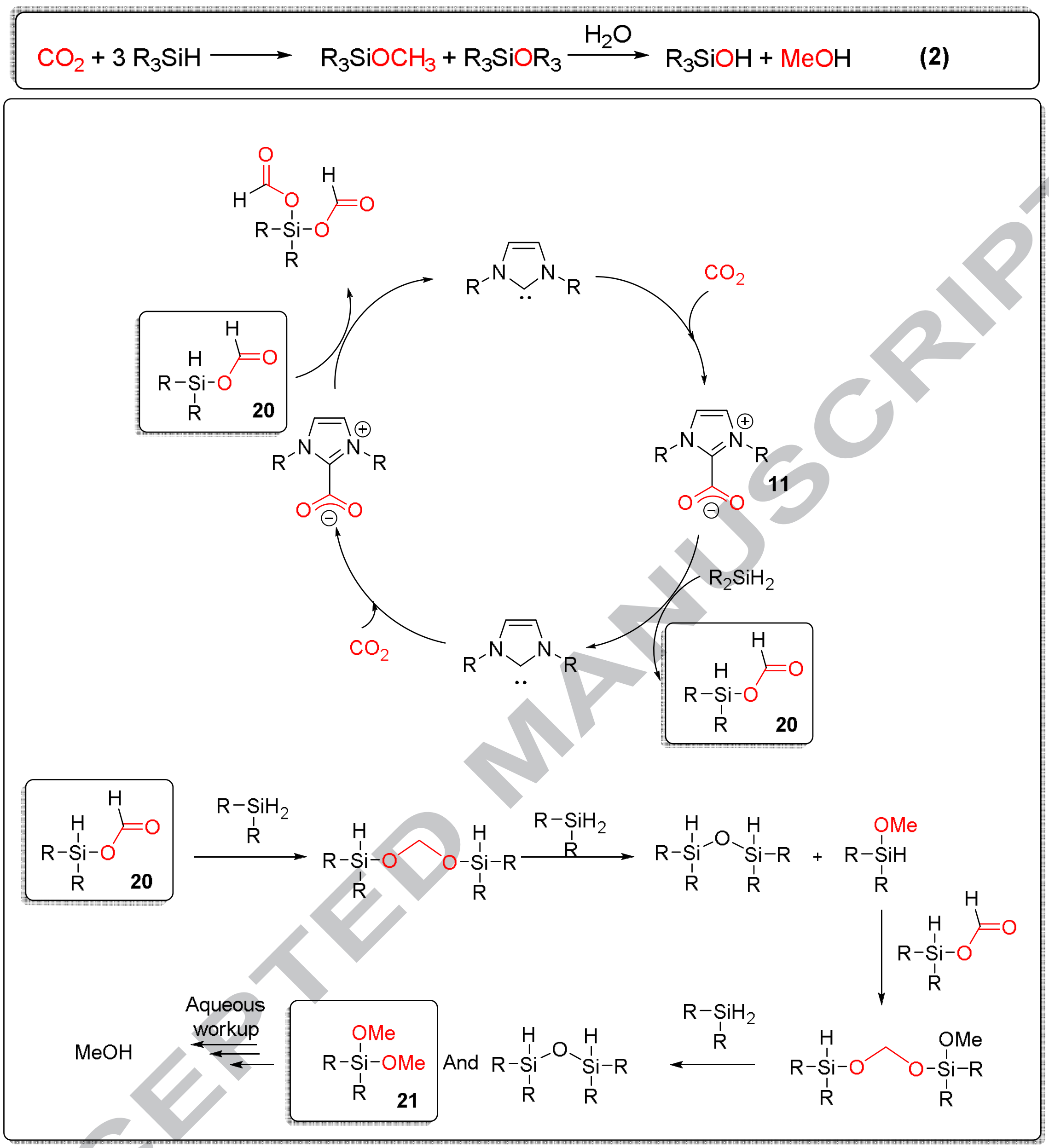


Figure 3. Tuning of the strength of CO_2 binding with N-heterocyclic carbenes. Plots of the T of CO_2 release *vs* dihedral angle between NHC and CO_2[35].

Although outside of the scope of the current discussion as it relates to an oxidative process, we would like to note an example of electrode-driven organocatalytic process[37]. Bodyston and coworkers report the preactivation of an aldehyde *via* a NHC organic fragment. The preactivation is then followed by an anodic process to electrochemically generate an oxidized intermediate than can react with an alcohol to form an ester.

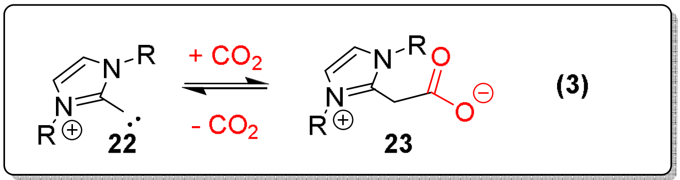
In the reductive regime, the organocatalytic reduction of CO_2 to methanol has now been reported by Riduan *et al* (Eq 2)[38]. The reaction is mediated by a free NHC binding the CO_2 and initial formation of an NHC-CO_2 adduct (**11**). The adduct has been shown to be able to undergo sequential reductions by the terminal reducing agent, the silane. Intermediate formates (**20**) and silanols (**21**) have been observed by mass spectrometry.



Scheme 5. Silane as a terminal reducing agent in NHC-catalyzed CO_2 reduction to methanol.

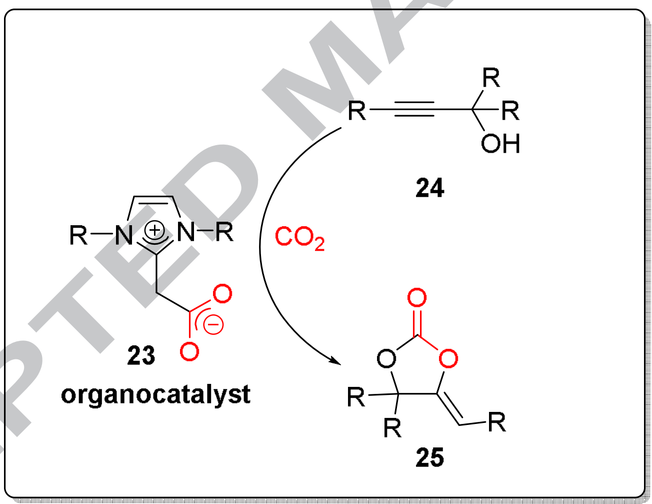
Upon aqueous workup, the terminal silanol reduced species is able to release methanol as a 6e$^-$ reduced *liquid* product. Mechanistic studies [39] [40] suggest that the limiting step in the chemistry is the formation of strong Si-O bonds. This provided a chemical opportunity for replacing the silane reducing agent with an electrode-generated reducing agent, shown to take the reduction of the NHC-carboxylate down to an 8e$^-$ reduced product, methane, as reported by Luca *et al*[41]. To the best of our knowledge, this is the first report of such a reductive transformation and we remain forward-looking to developments in the field.

3.3.2. N-Heterocyclic Olefin (NHO) Carboxylates and Catalysis



N-heterocyclic olefins (**22**) are a class of Lewis-basic species that have been highlighted for their ability to stabilize main group hydrides in usually low oxidation states[42]. In addition, borenium cation stabilization has also been shown[43]. Showing a similar behavior with the NHCs, they have been shown to be sufficiently Lewis-basic to react and bend CO_2 (Eq 3) to form adducts such as **23**.

NHOs have been shown to catalyze polymerization reactions[44]. Similar to the NHC chemistry in 3.3.1., NHO carboxylates have formed through productive CO_2-binding and have now emerged as competent catalysts for CO_2 transfer (Scheme 6). They were shown to react with propargylic alcohols (**24**) to form α-alkylidene cyclic carbonates in high yields (**25**)[45].



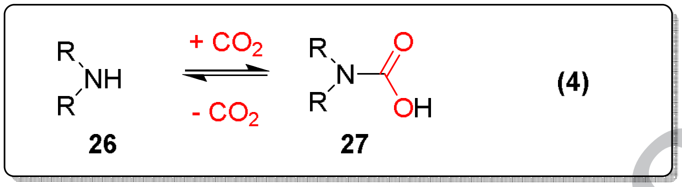
Scheme 6. N-heterocyclic olefin-catalyzed carboxylation of alkynes.

The authors note that the activity of NHO-CO_2 adducts is in some cases 200-fold when compared to the NHC-CO_2 analogues (Section 3.3.1). The hypothesis for the particular trend was the ability of the NHO-CO_2 to release the CO_2 fragment easily due to its less Lewis basic nature. This particular property may become an important factor in the development of electrode-driven processes.

3.3.3. Carbamates and Related Reductions (1)

Carbon dioxide has been shown to react with amines [46-48] (Eq 4, **26**) and related derivatives to form carbamates (**27**). The chemical reduction of carbamate-related species has been recently reviewed elsewhere[49]. Highly nucleophillic primary amines have been shown to react with CO2 to form urea derivatives in a formal 2e$^-$ reduction process[50].

The less-nucleophillic pyridines have also been shown to react with CO_2 anion radicals[51] to form carbamate anion radicals. This chemistry has been the protagonist of a series of electrochemical and photoelectrochemical studies for the pyridine-mediated conversion of CO_2 to chemical fuels[8, 52].

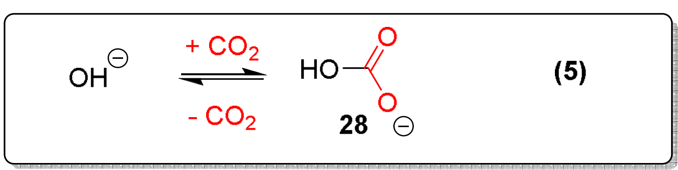


An important report in the field of CO_2 preactivation comes from Dyer and coworkers.[53] 6,7-dimethyl-4-hydroxy-2-mercaptopteridine, a N-containing commercially-available heterocyclic compound was shown to act as a mediator for the electrochemical reduction of CO_2 to methanol, albeit with modest faradaic efficiencies (10-23%). Mass spectrometry indicates that the chemistry may be facilitated by a carbamate formed *in situ*. Other observed products during the catalysis are formates and aqueous fomaldehyde. Reduction of 1-pyrrolyl and 1-indolyl carbamates to hemiaminals[54] has also been demonstrated electrochemically.

We believe that side chemical reactions between products of CO_2 reduction, particularly formaldehyde and formic acid under the conditions of electrocatalytic conversion may have important contributions to the products observed. For example, in an attempt to perform the electrochemical conversion of CO_2 bound to an amine preactivator under basic aqueous conditions, an Eschweiler- Clark [55] *chemical* reaction is favored to occur. This reaction may be responsible for observed product distributions. We highlight this type of transformation in Section 8.5.

3.3.4. Bicarbonates and Related Reductions

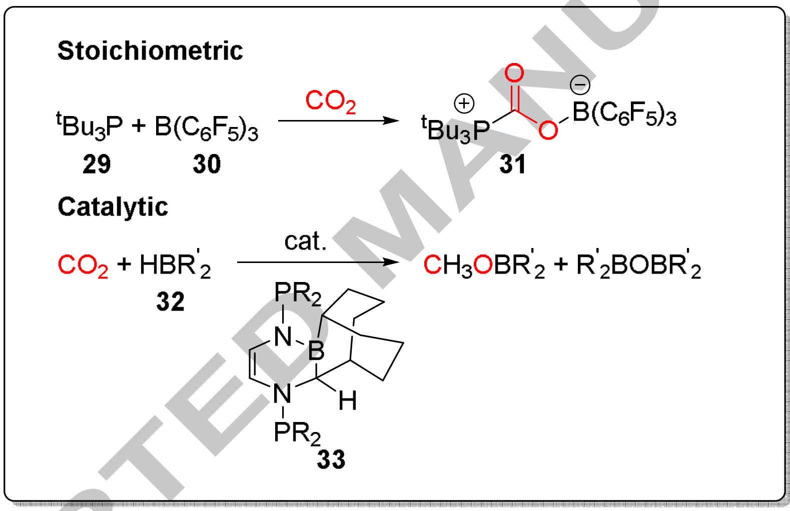
Hydroxide anions react with carbon dioxide in a similar fashion to amines and N-heterocyclic carbenes to form bicarbonate anions (Eq 5, **28**). This type of reactivity is of particular interest in the field of solar fuels, as several of the proposed solar-fuel devices involve aqueous conditions in basic media due to limitations on the anodic side chemistry of a solar-fuel device[1].



Bicarbonate reduction is an important discussion topic, as current solar-fuel device designs will likely rely on basic conditions. Under such conditions, the CO_2 concentration in an aqueous phase is increased, as CO_2 speciates in solution as bicarbonate [1]. Most excitingly a reversible bicarbonate/formate interconversion has been the protagonist of a recent report illustrating the concept of a formate battery[56]. This is an example of a Virtual Hydrogen Storage device [14, 57, 58] using CO_2 as a molecular framework for the storage of hydrogen equivalents as highlighted in a recent report[1].

3.4. Lewis-Acid/Base Activation and Catalysis

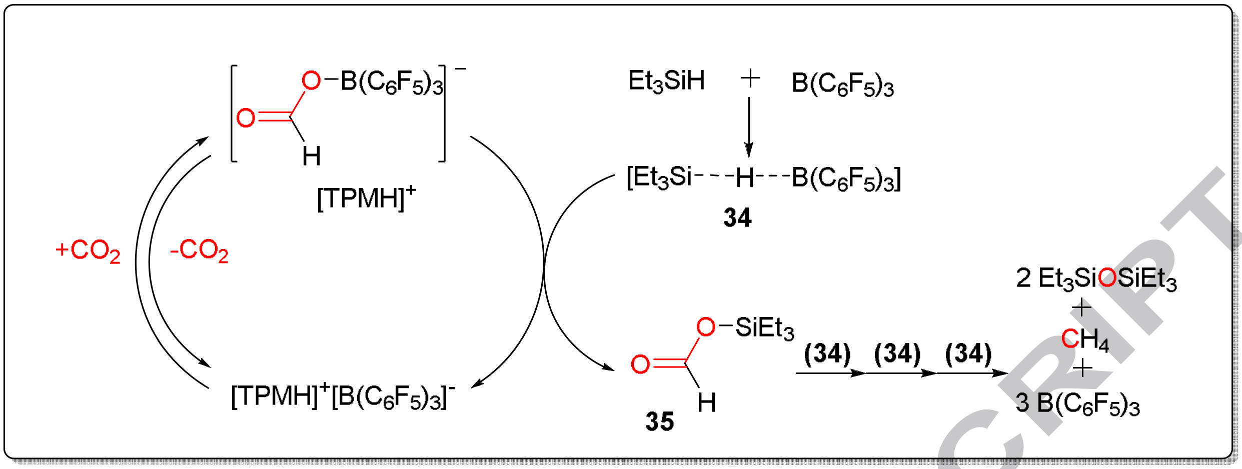
A Lewis acid, such as a borane, can poise the CO_2 molecule to more easily accept reducing equivalents, such as hydrides. (**30**). A Lewis base (**29**) is then able to aid in the formation of a CO_2 complex in the form of a $LB^+CO_2LA^-$ (**31**)[59]. In Scheme 7, such binding is demonstrated to occur with a phosphine Lewis Base and a borane Lewis Acid. Catalytic reductions of CO_2 to methanolic species have been shown with the help of phosphine-borane (**33**) binding and catalysis [60, 61] with a borane terminal reducing agent (**32**).



Scheme 7. Lewis acid-base activation and catalyzed reduction of CO_2 with phosphine boranes[60, 61].

In a similar fashion, aided by Frustrated Lewis-Acid/Base Pair (FLP), the selectivity for CO_2 reduction was shown to switch to a fully reduced 8e$^-$ product, methane, in the case of an amine-borane hydrosilylation [62] and aluminum-silane CO_2 reduction catalysis [63]. An important application of these FLPs is the activation of H_2 and subsequent use in catalytic hydrogenation reactions, [64] some of which involve carbonyl groups [65].

To illustrate a relevant chemical transformation, we describe a silane-borane FLP motif and subsequent CO_2 binding (Scheme 8, **34**). The initial binding and activation of CO_2 leads to the formation of a formate species (**35**). This event is followed by a cascade hydrosilylation reduction [60]. The frustrated Lewis pair between a borane and a silane has now been directly observed [66] and several instances of related asymmetric hydrogenation and hydrosilylation have now been reviewed[67].



Scheme 8. Lewis acid-base activation and catalyzed reduction of CO_2 with silane boranes.

3.5. CO_2 Binding to Metal Centers

3.5.1. Binding Modes

Next in our discussion, we illustrate some binding modes observed in organometallic and coordination compounds and relate these modes with the binding of organic molecules to CO_2. An extensive discussion of such binding has been made available by Gibson [68] and Leitner [69] and we illustrate some structural examples in Figure 4.

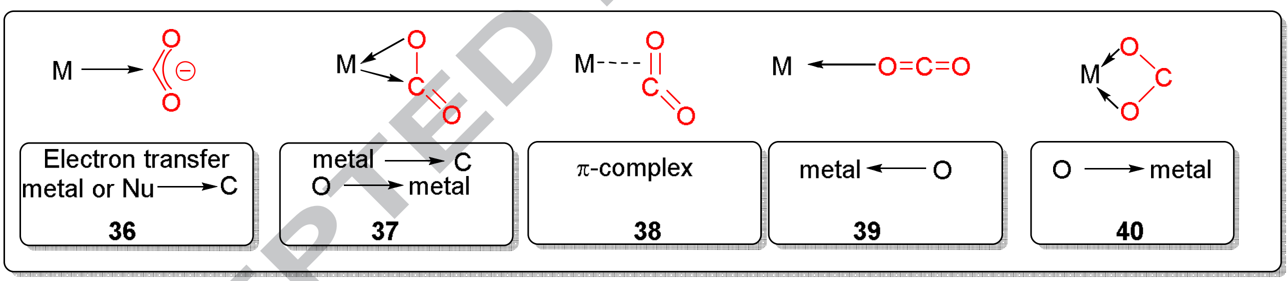
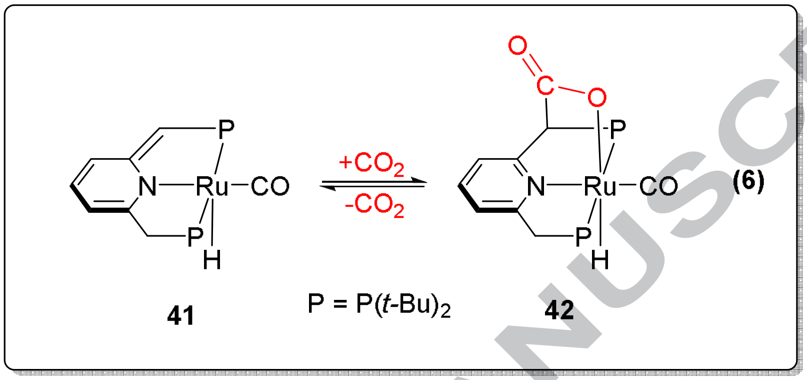


Figure 4. Binding Modes of CO_2.

There are five observed binding modes of CO_2 to metal centers (Figure 4). The coordination type depends on the nature of the metal, on the oxidation states and, consequently, on the available orbitals of the metal center. The explicit coordination environment of the metal complex also plays an important role. If the metal complex has available empty orbitals, coordination with donation of electron density from the O ligand will be possible (end-on for **37**, **39** and **40** and side-on for **38** in Figure 4). CO_2 binding to Lewis acidic metals usually involves coordination through the oxygens and depending on the available anchoring sites and oxidation states, it can occur η^1-CO_2 (**39**) or η^2-CO_2 (**40**).

If the metal complex has a low-valent nucleophilic site, then CO_2 coordination occurs as an η^2-CO_2 complex with the metal bound to the central carbon to form a carboxylate (**36**). This particular type of coordination is also observed in the presence of organic nucleophiles as described in Section 3.3 and is of particular interest in the field of electrocatalysis for CO_2 reduction with molecular species (section 3.4.3). The central C-binding mode (**36** in Figure 4) of CO_2 is the protagonist of several of the state-of-the art electrocatalytic processes for CO_2 conversions at metal centers[1, 70]. An example of such reactivity is given in Section 3.5.3.

3.5.2. Metal *vs* Ligand Coordination and Redox-Active Ligands[71]

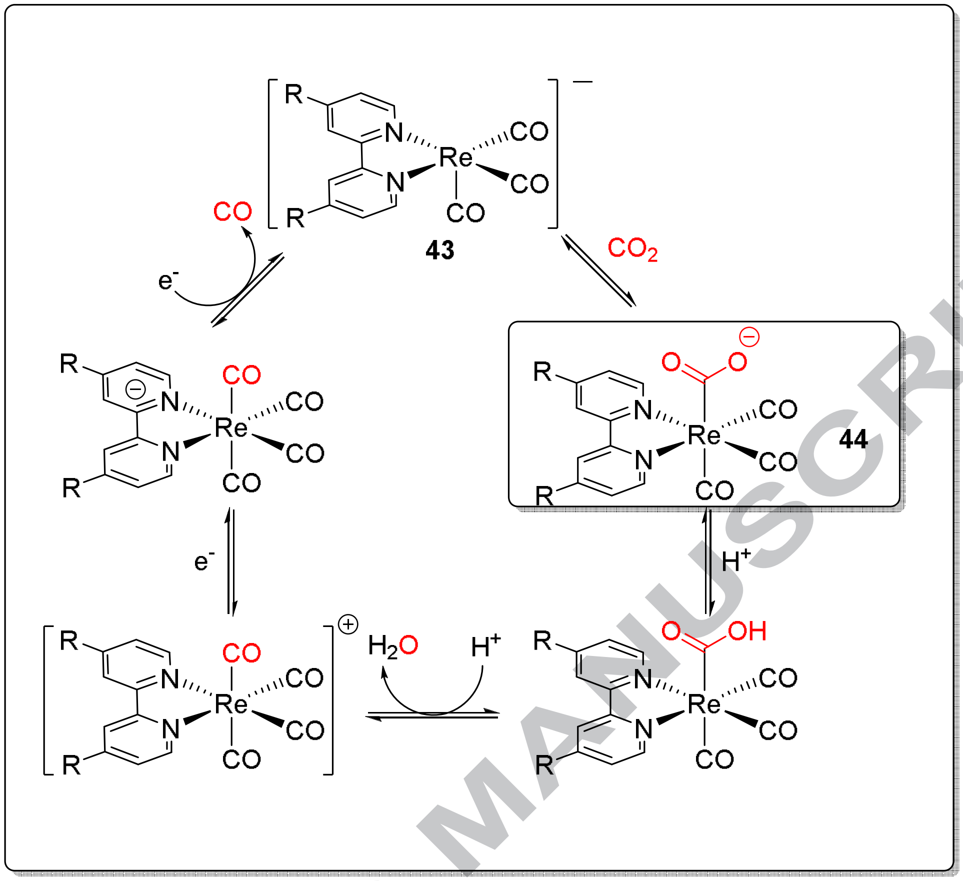


A topic of great interest in the catalysis community, the concept of redox-active actor ligands, plays an important role in CO_2 coordination at metal centers and has extensively been described elsewhere[71]. We give one example of ligand participation in CO_2 binding to the organic fragment of a Ru complex with a redox-active ligand (Eq 6).

Milstein and coworkers have now shown that the presence of a nucleophilic redox-active diphosphine ligand on a Ru center (**41**) facilitates the indirect reduction of carbonates under hydrogenation conditions[72]. Specifically, the first step in this chemistry is the coordination of CO_2 to the relevant metal complex yields an intermediate with the CO_2 fragment C-bound to the nucleophilic ligand center and O-bound to the Ru in a side-on fashion (**42**).

3.5.3. Electrocatalytic CO_2 reduction *via* Metal Carboxylates

As CO_2 electrocatalysis [1] for the formation of fuels remains a topic of great interest, we illustrate one of many examples of CO_2 binding to a reduced metal complex; specifically, we make note of an important intermediate in the Re-catalyzed conversion of carbon dioxide to CO.

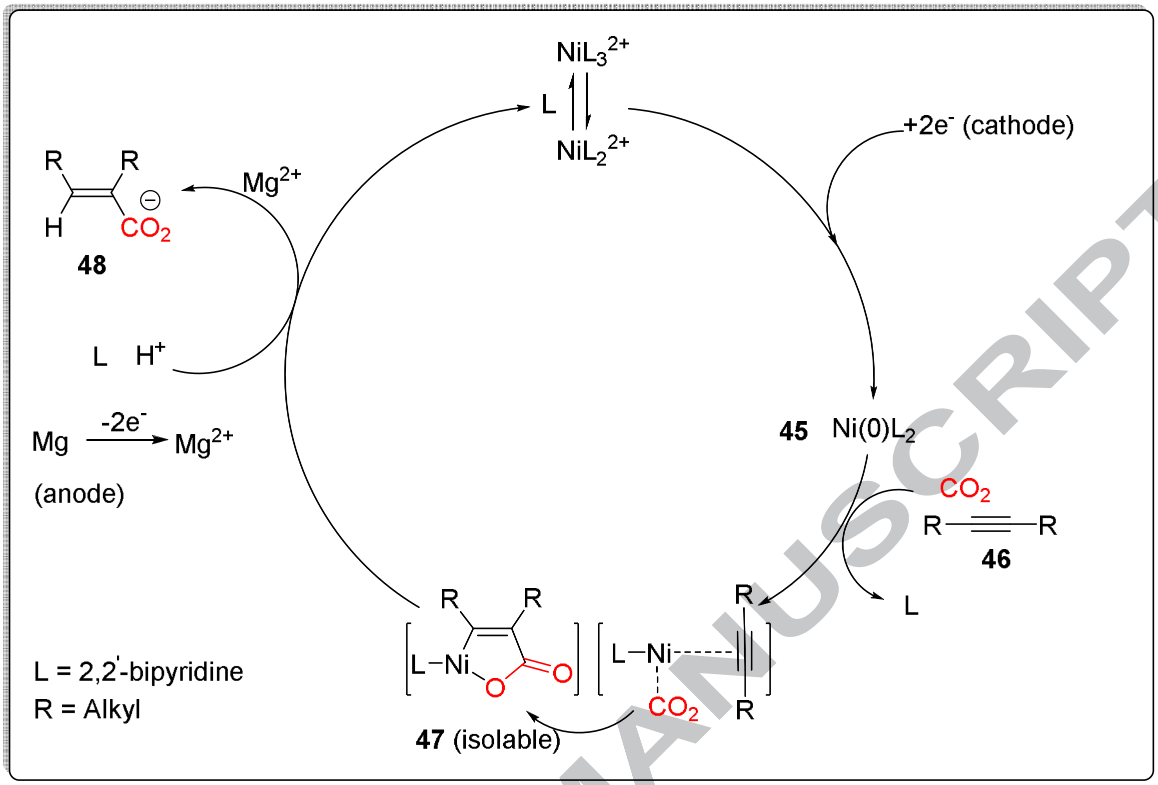


Scheme 9. Electrocatalytic CO_2 reduction cycle with $Re(bpy)(CO)_3X$.[70]

In the current catalytic understanding, binding mode **36** occurs after the reaction of CO_2 with a nucleophilic reduced complex **43**. This carboxylate **44** can then be protonated and further reduced in a catalytic cycle as shown in Scheme 9. A Mn variant of this chemistry has also been reported [73] and specifically, the reduction of a $(bpy)(CO)_3Mn^ICO_2H$ was observed *via* IR-spectroelectrochemistry[74].

3.6. Electrocarboxylation Reactions

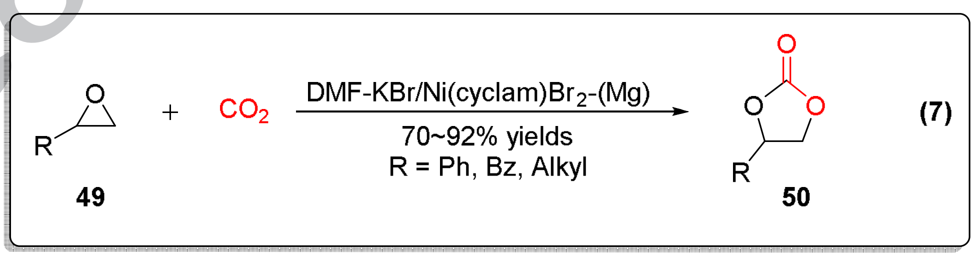
An electrocarboxylation reaction is the reaction of CO_2 with an organic molecule to form carboxylic acids under electrochemical conditions[75]. The preparative and large-scale implementation of such reactions has been extensively studied and the results have been described in detail elsewhere[76].



Scheme 10. Electrocarboxylation of alkynes *via* Ni $(bpy)_2{}^0$ in a single-compartment electrolysis cell. [75]

To describe this type of electrode-induced CO_2 preactivation, we give an example of electrochemical incorporation of CO_2 into unactivated alkynes (**46**). This reaction has been successfully mediated by an electro-generated $Ni(bpy)_2{}^0$ (**45**) in a single-compartment electrolysis cell to yield α,β- unsaturated carboxylic acids (**48**, Scheme 10). In the case of 4-octyne, a nickleacycle (**47**) was isolated and characterized[75].

A further example of CO-selective CO_2-reduction molecular electrocatalyst is $Ni(cyclam)^{2+}$[77, 78]. Interestingly, $Ni(cyclam)^{2+}$ has also been shown to be an effective mediator for the electrosynthesis of cyclic carbonates (**50**) from epoxides (**49**) and CO_2 (Eq 7).



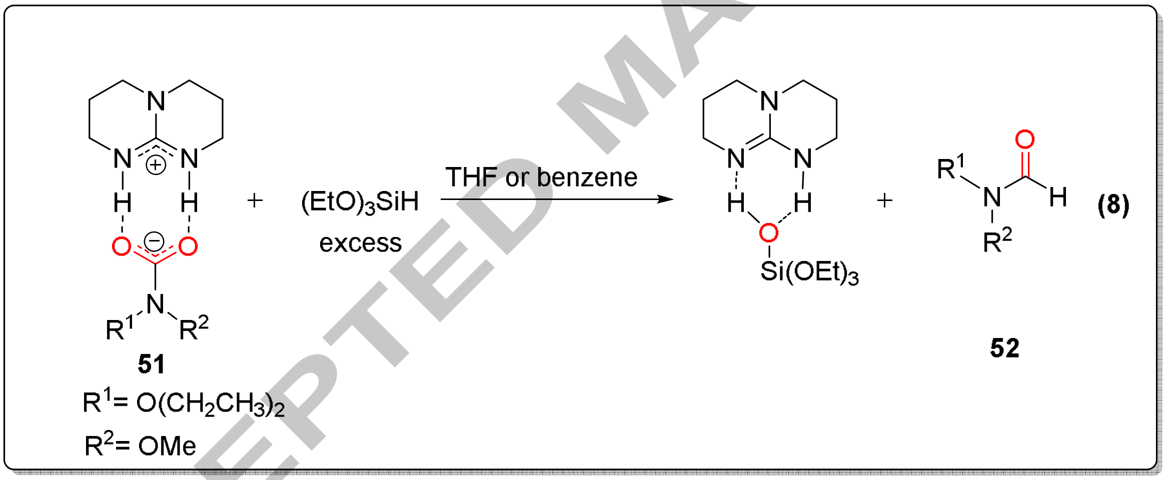
4.0. Reduction of Carboxylic and Carbamic Acids to Aldehydes

4.1. Carboxylic Acid Reductase

The reduction of carboxylic acids to aldehydes can be performed enzymatically by carboxylic acid reductase(CAR)[79, 80]. The enzyme is able to convert non-activated carboxylates to the corresponding reduced aldehydes without overreduction to the corresponding alcohols[79, 80].

Specifically, studies on recombinant CAR have demonstrated conversion of fatty acids (C_6-C_{18}) as well as benzoic, vanillic, and ferulic acids to their corresponding aldehydes. The broad substrate specificity of CAR, in combination with an aldehyde reductase co-enzyme, has been studied as possible metabolic route for the biosynthesis of fuels and commodity chemicals. Since the work is biochemical in nature, it falls outside of the scope of this discussion, although it sets an important precedent for the chemistry discussed in Section 9.

4.2. Chemical – Carbamate Reductions



The preactivation of CO_2 with amines was described in Section 3.5.3. In a recent study, 1,5,7-Triazabicyclo[4.4.0]dec-5-ene was shown to catalyze amine hydroformylation (Eq 8). The CO_2 fragment is first stabilized and activated into a zwitterionic carbamate (**51**). This species is able to undergo reductive hydrosilylation to the corresponding aldehyde species (**52**).

An in-depth study on this type of organocatalytic formylation of morpholine using CO_2 and silanes is now in the literature[81] [60]. This chemistry comes as an alternative to previous methods employing Ru catalysts [82, 83]. If the terminal silane reducing agent would be electrochemically

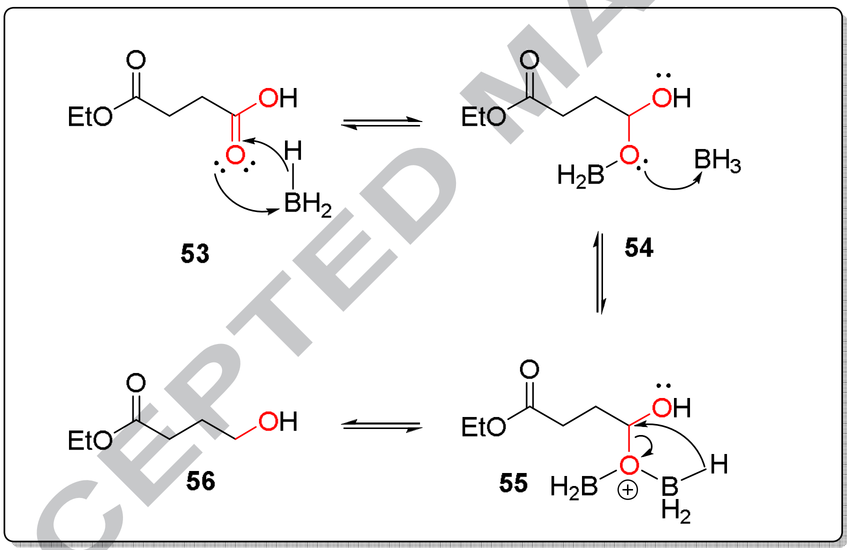
4.3. Electrochemical

Although the reduction of a free carboxylic acid directly to an aldehyde product has not been reported to the best of our knowledge, we point out the conversion of carboxylic acid derivatives such as esters to the corresponding aldehydes under electrochemical conditions. Alkylbenzoate esters and amides, for example, have been cleanly reduced to the corresponding aldehydes with the help of chlorotrimethylsilane in up to 64% yields[84]. Acyl halides and aliphatic amides have also been converted to aldehydes, albeit in modest yields[85].

5.0. Reduction of Carboxylic Acids and Carbamates to Alcohols

5.1. $LiAlH_4$, $NaBH_4$ and BH_3

Lithium aluminum hydride ($LiAlH_4$), sodium borohydride ($NaBH_4$) and borane (BH_3) are common reducing agents used in organic transformations involving the conversion of carboxylic acids to the corresponding primary alcohols. Each of these three reducing agents operates by a different mechanism for their respective reductions. The choice of reducing agents for a particular transformation at hand is generally a topic covered in standard organic coursework. As such, we limit our discussion to just one example and illustrate the reduction of a carboxylic acid by BH_3.



Scheme 11. Carboxylic acids reduction to alcohol with boranes.

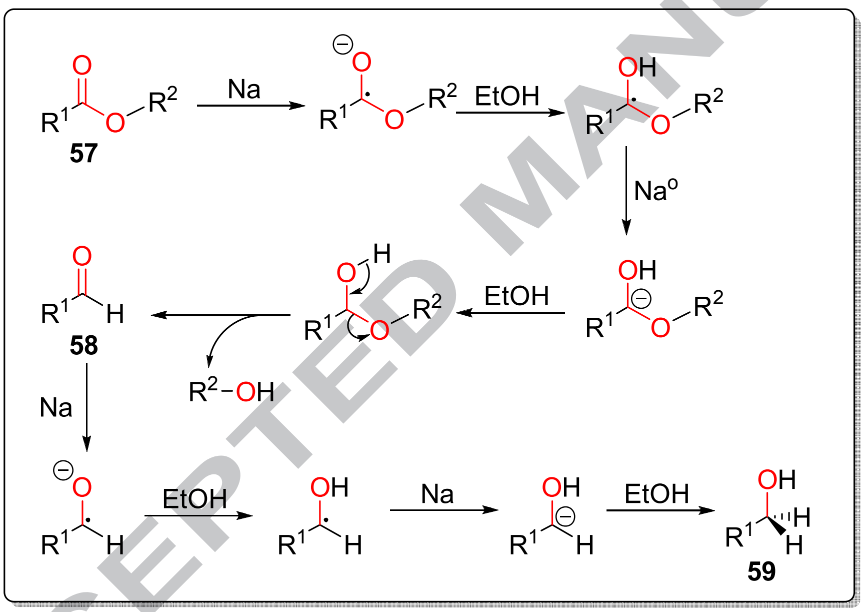
The mechanism of reduction of carboxylic acids to alcohols with BH_3 occurs through the addition of a first borane equivalent across a C=O bond (**53** → **54**) followed by the coordination of a second borane equivalent to the newly-formed alcohol moiety (**54** → **55**) and elimination of BH_2OBH_2 unit to lead to the formation of the primary alcohol product (**56**) (Scheme 11).

The electrochemical generation reducing agents that can accomplish transformations commonly performed by lithium aluminum hydride or borohydride species is not well-understood. Consequently, further electrochemical studies on the generation of such reducing agents will likely lead to new chemistries in the future.

5.3. Bouveault-Blanc Reduction[86, 87]

The Bouveault-Blanc reduction of aliphatic and aromatic esters is a method for the reduction of carboxylic acids to alcohols *via* a 1e$^-$ reduction with a group IA metal such as sodium[87, 88].

The traditional Bouveault-Blanc reduction is the sequential Na reduction of a carboxylic acid derivative (**57**) in protic medium as described in Scheme 12. The utility of this chemical its is rather limited as it occurs under extremely harsh reductive conditions with poor functional group tolerance and selectivity. The product of such a reaction is usually a mixture of alcoholic products. In a milder set of conditions, an ester can be reduced by SmI_2 in a polar aprotic solvent such as hexamethylphosphoramide (HMPA) instead of Na.



Scheme 12. Bouveault-Blanc Reduction Na reduction of carboxylate derivatives to primary alcohols.

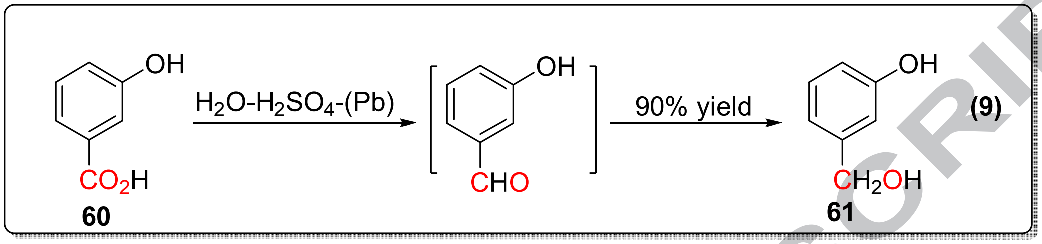
5.4. Electrochemical Bouveault-Blanc Reduction

Since the mechanism of this transformation occurs via sequential 1e$^-$ reductions, it was translatable to electrochemical conditions. Lam and coworkers have now adapted this chemistry to an electrode-driven process [89]. Study of reaction conditions have shown that the single-electron process occurs optimally in DMF and NMP, as THF and MeCN have reactivity issues due to the relatively narrow potential windows in the conditions. Temperature and electrode material effects have also been observed and yields of up to 50% were observed on Carbon electrodes at 130 ºC in an electrolysis under reflux conditions.

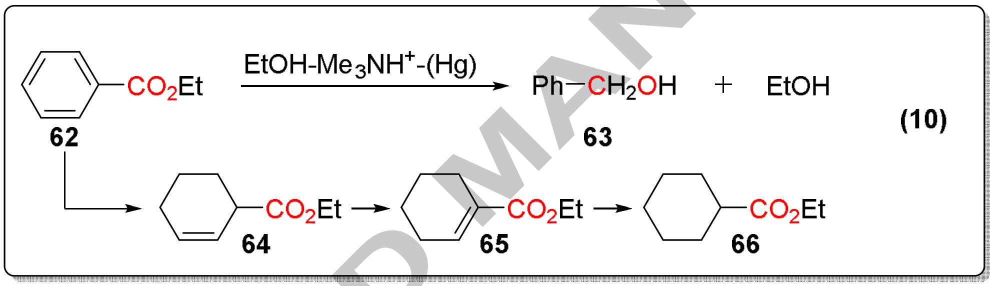
5.5. Reduction of NHC Carboxylates with Silanes – Methanol Production [39] [40]

This particular chemistry was described in Section 3.3.1. The observed chemistry is limited by the strong Si-O bond formed**[40].**

5.6. Other Electrochemical Reductions [75]



Aromatic carboxylic acids (**60**) and ester derivatives (**62**) have been shown to be electrochemically reduced under cathodic conditions to the corresponding benzyl alcohols (**61** and **63** respectively) as depicted in Eq 9 and 10. Notably, the reduction also proceeds to break the aromaticity of benzoic acid in ethanol[75].



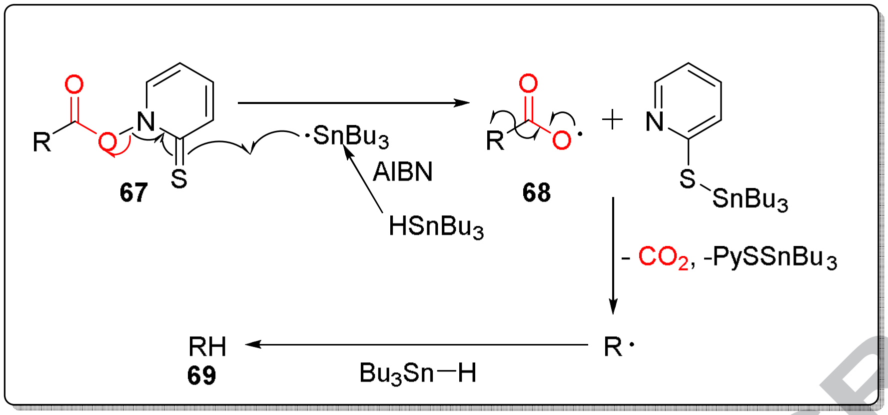
6.0. Reduction of Carboxylic Acids to Alkyls

6.1. Carboxylic Acid Reductase Tandem Catalysis

In section 4.1 we briefly touch on the reduction of carboxylic acids to aldehydes. In conjunction with an additional reducing enzyme, the intermediate aldehyde can be further reduced to an alkane[79, 80].

6.2. Barton McCombie Decarboxylation and Electrochemical Variant[90, 91]

The Barton-McCombie decarboxylation is the radical-induced loss of CO_2 from a thiohydroxamate ester (**67**) as shown in Scheme 13. A carboxylic acid can be derivatized to such an ester. In the presence of a radical initiator such as AIBN and a hydrogen donor such as trialkyl tin hydride, the formed carboxylate radical **68** decomposes with loss of CO_2.

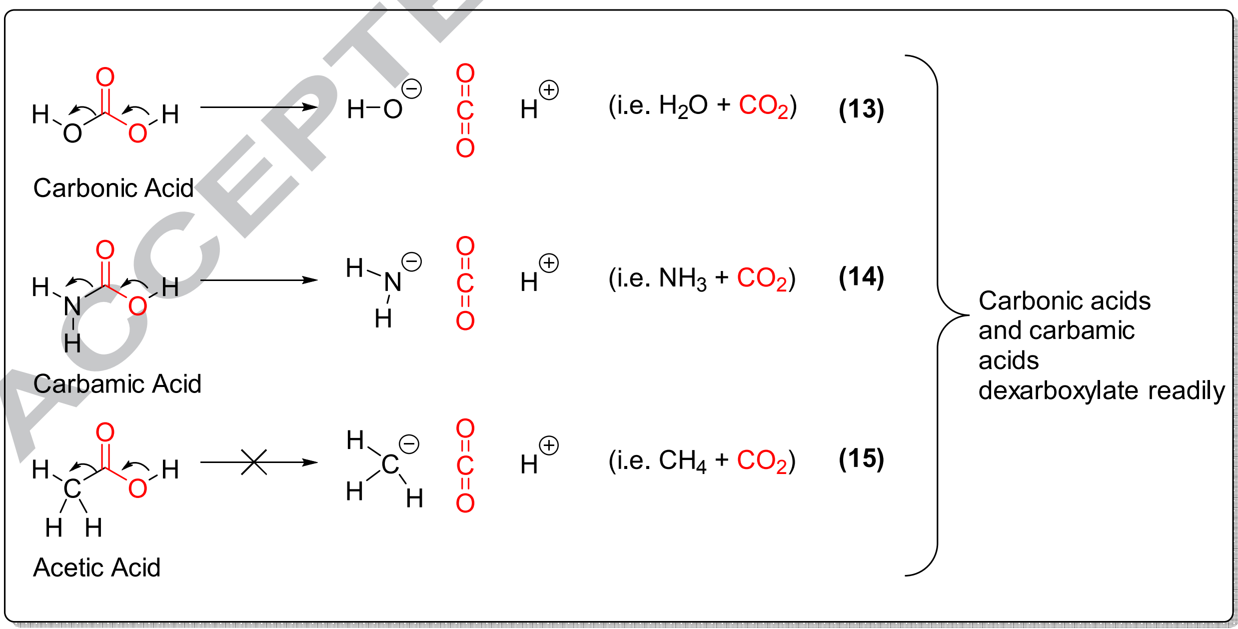


Scheme 13. Mechanism for the Barton McCombie Decarboxylation reaction.

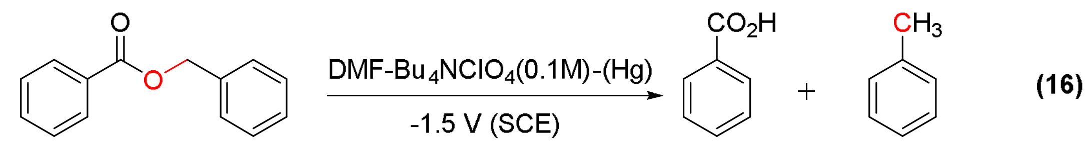
Carbonic and carbamic acids (Eq 13 and 14) are known to decarboxylate rather easily, whereas aliphatic acids do not (eq 15).

There are several synthetic applications of the acid decarboxylation, although a drawback of these conversions is the use of highly-toxic tin reagents. An electrochemical variant of this transformation was observed during the electrolysis of 1-isoquinoline carboxylic acid [92].

A series of related radical halodecarboxylatios transformations are known.: the Hunsdiecker-Borodine [93-95] and the Simonini reaction[96]. These transformations convert carboxylate salts into the corresponding alkyl and aryl halides in the presence of oxidizing Br_2 and I_2 respectively. If X_2 (X=Cl, Br or I) is produced in an anodic process during an electrolysis, these reactions may lead to productive halodecarboxylation chemistries in the presence of carboxylic acid derivatives if migration of the anodic species to the cathode occurs.



6.3. Electrochemical[75]



50% 47%

70 71 72

This particular type of conversion is important for historical reasons, as it was the first example of electrochemical transformation ever reported. In 1834, Faraday reported oxidative decarboxylative coupling of acetic acid to ethane as a $2H^+$, $2e^-$ process[97]. Years later, Kolbe reported a generalized version of Faraday's experiments, known today as the Kolbe electrolysis[98].

As far as reductive processes are concerned, the Barton Decarboxylation remains state-of-the-art in the field, although benzylbenzoate (**70**) has been converted to benzoic acid (**71**) and toluene (**72**) (Eq 16). This particular reduction is likely a reduction of the alcohol portion of the ester and as such, it counts as a reduction of an alcohol to an alkyl rather than as a decarboxylation event.

Another example of reduction of a carboxylate species to the corresponding alkyls is the selective electrochemical conversion of CO_2 to methane as reported by Koval and coworkers [41]. In this work, the NHC-preactivation highlighted in Section 3.3.1 was utilized to gain access to an $8e^-$ reduced product: methane. The CO_2 is first converted to a zwitterionic carboxylate by reaction with a nucleophillic carbene. The CO_2-adduct formed in this reaction was then exposed to reductive conditions in an electrochemical system in the presence of a Ni mediator in the presence of protons to effect the reductive chemistry.

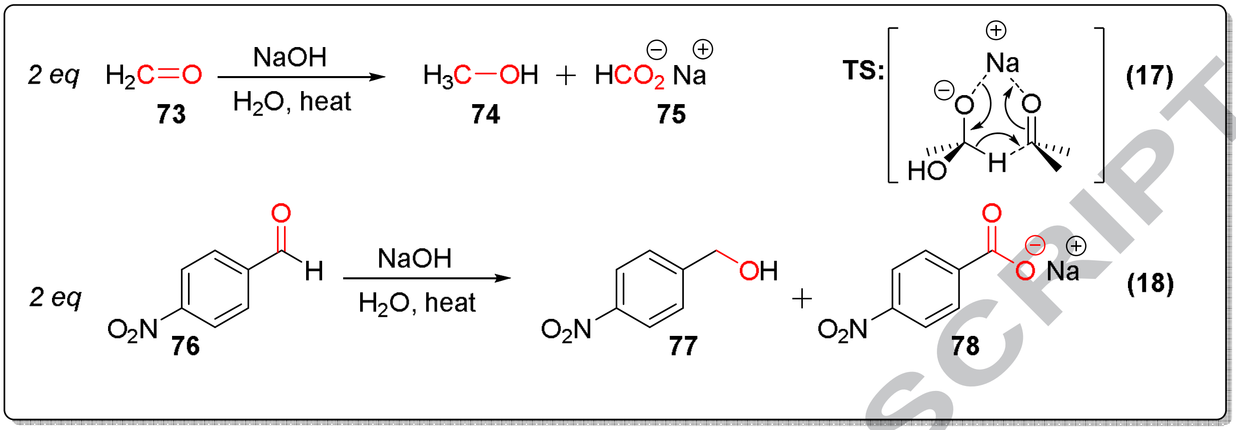
7.0. Reduction of Aldehydes to Alcohols

7.1. $NaBH_4$ and $LiAlH_4$

We briefly described the reduction of carboxylic acids in Section 5.1. The reduction of aldehydes to alcohols is a repetition of the last step of the conversion of carboxylic acids to primary alcohols.

7.2. Crossed Cannizzaro Reaction: Formaldehyde as a Reducing Agent[99, 100]

The Cannizzaro Reaction is a transformation specific to aldehydes without an available α-H *ie* formaldehyde (**73**) or benzaldehyde and derivatives (**76**). In the presence of strong basic conditions such as NaOH (Eq 17 and 18), two equivalents of an aldehyde can undergo an intramolecular H transfer (Eq 17 TS) in which one aldehyde molecule is oxidized to a formate and another molecule is reduced to the corresponding alcohol. Taking advantage of the rate of this reaction, high yields of any alcohol-reduced products can be obtained by using an excess of formaldehyde, as the oxidation of formaldehyde to formic acid is a favorable process. This process of using formaldehyde as a reducing agent is called the Crossed Cannizzaro reaction. A solvent-free variant of this reaction has been reported[101].



This particular transformation may become an important reaction in the field of solar fuels, as formaldehyde, a product on the CO_2 reduction pathway to methanol and methane, can *chemically* disproportionate under basic and thermal conditions to two different products, thus altering the product distributions. Thermal contributions to productive chemistry in electrochemical transformations for CO_2 reduction that can occur from resistive heating or illumination have been the subject of a recent report[102].

7.3. Silanes, [103] Boranes[104] and NHC Boranes[105]

In this section we enumerate some organocatalytic reduction chemistry with silanes and boranes as terminal reducing agents, as the transformations may become amenable to electrochemical conditions.

In a recent report, the hydrosilylation of carbon-heteroatom double bounds has been demonstrated in the presence of borohydride catalysts. Trace amounts of $LiHBEt_3$ and $NaBH_4$ have given high activity and good yields. In the case of this particular transformation, DFT calculations suggest the presence of a hypervalent Si intermediate[106, 107].

The activation of diphenylsilane by trace amounts of imidazolium salts (NHC precursors) has now been the protagonist of carbonyl reduction chemistry[103]. A similar hypervalent silicon active species has been invoked in the transformation, as the silicon intermediate can have strong Lewis acidic properties and also act as a strong hydride donor.

Pinacolborane has also been shown to catalytically reduce carbonyl compounds in the presence of NaO*t*Bu as catalyst[104]. The active reducing agent in this reaction has been shown to be an *in-situ* generated trialcoxyborohydride.

Aldehyde reduction has also been demonstrated with 1,3-dimethylimidazol-2-ylidine trihydridoborane as the active hydride donor[105]. In the presence of silica gel, the conversion to alcohols occurs smoothly and in good yields. Excitingly, this particular reactivity is specifically selective for aldehydes. Ketones are not reduced in the course of this chemical transformation.

7.4. Electrochemical Reduction: Reductive Dimerization[75]

The reductive electrochemistry of aldehydes is plagued with selectivity issues related to polymerization reactions[108, 109]. However, the key to long-sought productive C-C coupling reactions leading to the production of long-chain alkane fuels from CO_2 may lie in this particular reductive regime. Several examples of well-controlled polymerizations have been reported and we remain forward-looking to developments in the field[110, 111].

Of particular note in this direction is the work of Kanan *et al* [112] where the reduction of CO over nanocrystalline Cu yielded C_2 and C_3 products such as ethanol, acetate and *n*-propanol. A formyl radical coupling may be involved in the process.

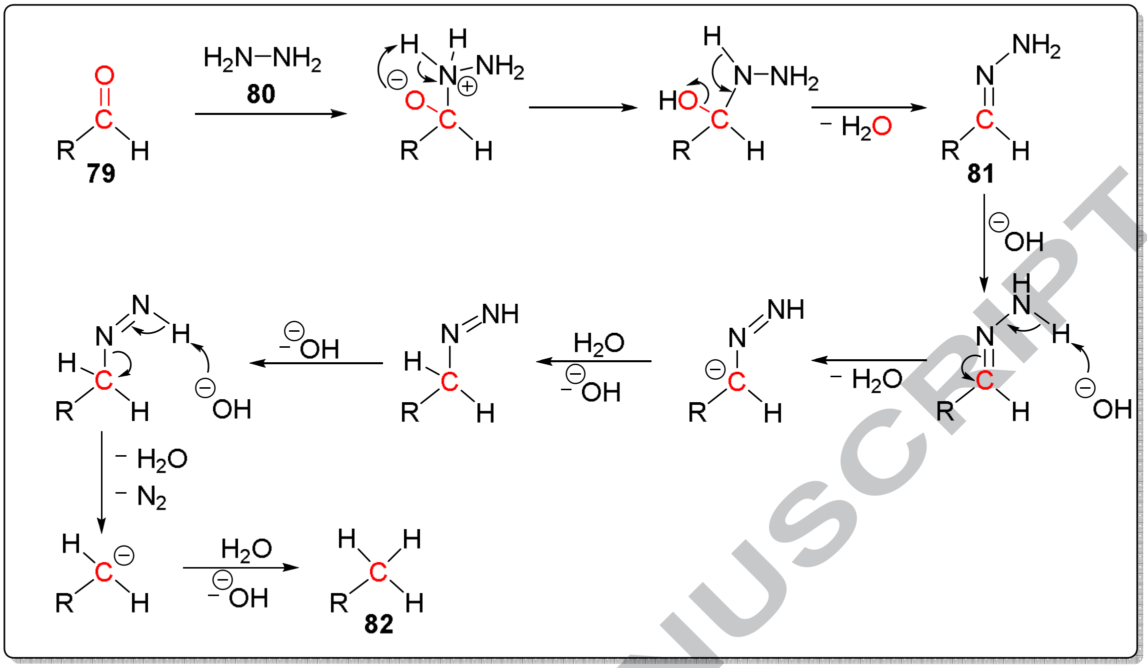
7.5. Electrochemical Reduction on Cu Electrodes

Interestingly, a report of organic reduction of aldehydes over Cu shows great selectivity for alcohols without the formation of multimeric products[113]. The undivided electrolysis cell was connected to a 6V battery and was used to demonstrate the conversion of aliphatic and aromatic aldehydes to the corresponding alcohols.

8.0. Reduction of Aldehydes to Alkyls

8.1. Wolff–Kishner Reduction [114]

An aldehyde (**79**) reacts with hydrazine (**80**) to form a hydrazone (**81**). After the carbonyl activation step, under basic alcoholic conditions and heat, hydrazones can decompose to form the corresponding alkyls (**82**). The overall reaction sequence is known as the Wolff-Kishner reaction (Scheme 14). High temperatures are required, and the transformation is incompatible with hydrolysis-prone substrates such as esters, lactams, lactones, amides, etc. Examples of side-reactivity include the incomplete reduction of the carbonyl group to an alcohol rather than the alkane, as well as elimination reactions and double-bond isomerizations**[114].**



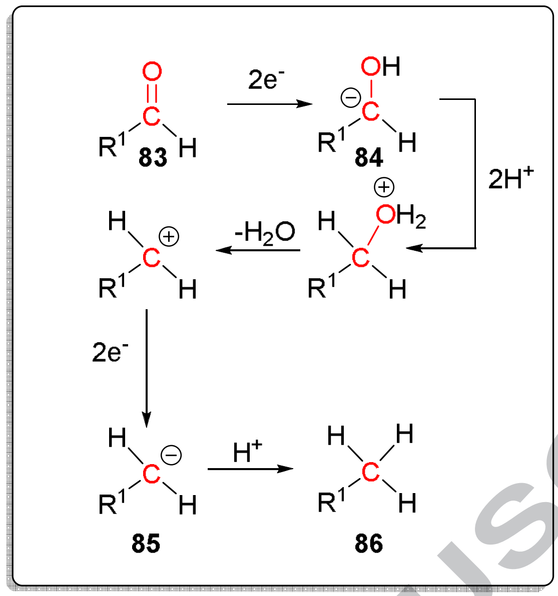
Scheme 14. Wolff–Kishner Reduction Mechanism.

8.2. Caglioti Reaction: Reduction of Tosylhydrazones[115]

A modification of the Wolff-Kishner Reduction, the Caglioti reaction occurs *via* the reduction of a tosylhydrazone[116]. Such reduction can be performed with mild borane reducing agents such as catecholboranes. Tosylhydrazide intermediates have been isolated[117] [118]. Other compatible reducing agents are lithium aluminum hydride [119] and the milder sodium cyanoborohydride[120].

8.3. Clemmensen Reduction[121]

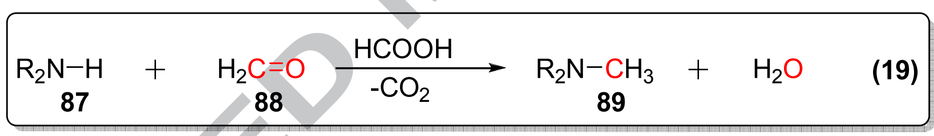
The Clemmensen Reduction is the conversion of carbonyl compounds to the corresponding alkanes under harsh acidic conditions. The original report employed Zn/Hg amalgam, a 2e$^-$ reducing agent. The aldehyde (**83**) undergoes two sequential 2e$^-$ reduction steps through a dehydration step and two anionic intermediates **84** and **85**.

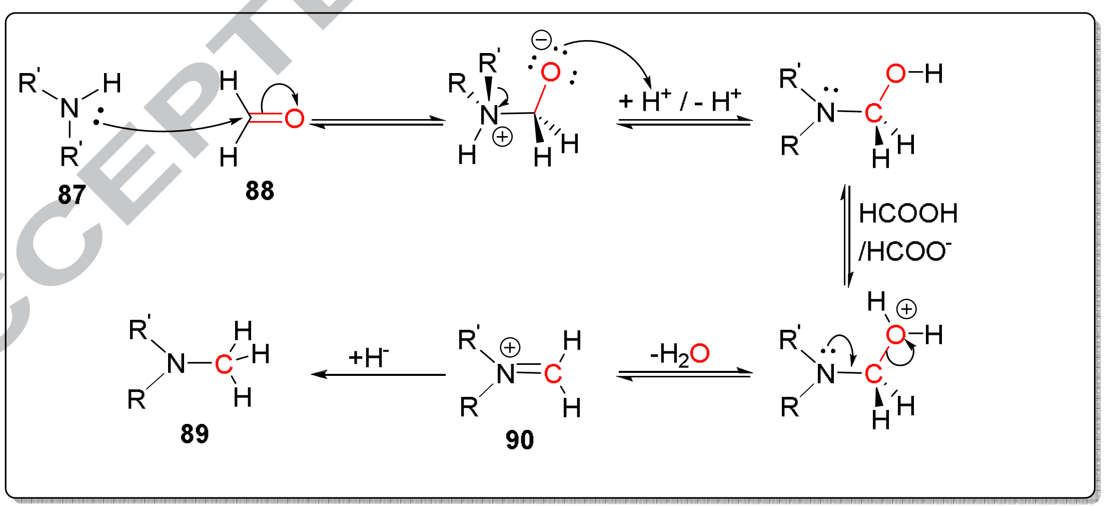


Scheme 15. Mechanism for the Clemmensen Reduction.

An interesting report highlights fuel production with Zn from formaldehyde *via* a Clemmensen reduction[122] [123].

8.5. Eschweiler-Clarke Reaction: Formaldehyde as an Oxidizing Agent[55]





Scheme 16. Mechanism for the Eschweiler-Clarke reaction.

The Eschweiler-Clark reaction is a reductive methylation reaction using an aldehyde (**88**) as an oxidizing agent. Eq 19 is an example of such a reaction with formaldehyde as a methylating agent for the corresponding amine (**87**).

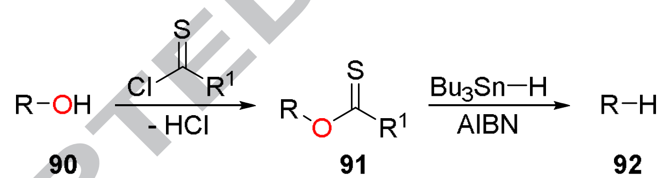
The reaction proceeds *via* the formation of an iminium ion (**90**) from the corresponding aldehyde and amine starting materials. In the presence of formic acid as a reducing agent, the iminium is reduced to the corresponding methylamine. The reaction is an overall reductive amination.

This type of chemical transformation may come into play in attempts at using amines as pre-activating /bending agents for the capture of CO_2 as carbamates as described in Section 3.3.3. Upon the reduction of carbamates, both formaldehyde and formic acid could be possible reduction products under the electrochemical conditions. In the presence of heating from electrolytic cell resistance or illumination in the case of possible photochemical experiments, non-faradaic Eschweiler-Clark reactivity can lead to the formation of methylated intermediates.

The observed methanol products in the electrocatalytic reduction of CO_2 in the presence of mercaptopteridine[53] could be the product of chemical hydrolysis of an N-methyl intermediate under the electrochemical conditions. Independent isolation and electrochemical characterization of specific chemical intermediates could provide a rigorous reactivity assessment of chemical entitites performing the observed transformations.

9.0. The Reduction of Alcohols to Alkyls

9.1. Barton-McCombie Deoxygenation[124]



(20)

The Barton McCombie Deoxygenation reaction is a radical-induced process that replaces the functional group of an alcohol (90) with hydrogen (Eq 20) to form an alkane (**92**). As such, it employs a H donor, usually a SnH, akin to the terminal reducing agent used in the decarboxylation reaction carrying the same name (Section 6.2). The first step in this transformation is the formation of a thioxoester derivative of the starting material, which can then undergo reduction with the tin reducing agent. The downside of this chemistry is the use of highly toxic tin reagents.

In recent reports, a photoredox process has been reported[125]. In a similar vein, the Cu-catalyzed reduction of alkyl triflates to the corresponding alkane, has also been reported[126]. Applications in total synthesis of this reaction have been reviewed by Faghihi and coworkers[127].

Several other deoxygenation methods have been reported and have been reviewed elsewhere[128, 129]. For the purpose of the current discussion we describe one electrochemical instance of such transformation in the following section.

9.2. Electrochemical methods

Shono has long reported the cathodic deoxygenation of mesylates as an alternative to liquid ammonia reductions of mesylates and triflates[128, 130]. The electrochemical method was attractive in that it had a good functional group tolerance: tolerating carboxylic acids, nitriles, olefins and epoxide functionality. Unfortunately electrolytic methods have not yet been adopted as a mainstream tool of organic synthesis.

10. Conclusion

Although a long-standing interest for many decades, the field of CO_2 reduction has not yet advanced to the stage of technological implementation. From an organic chemistry perspective, the solar fuels field will likely contribute a wealth of knowledge regarding the electrochemical generation of selective and functional-group tolerant reducing agents. As such, efforts in the electrochemical conversions of CO_2 to solar fuels may provide mild conditions for transformations related to carboxylic acids and intermediates.

CO_2 capture and subsequent reduction chemistry has unfortunately not yet been fully elucidated in terms of electrochemical regimes and we remain mindful of coupled chemical processes related to the chemical reactivity of possible intermediates. We look forward to the concept of chemical preactivation of CO_2 as an energy–relevant molecule as we propose that these transformations could be approached as an exercise in the electrochemical reduction of carboxylates and related further-reduced species.

Acknowledgements

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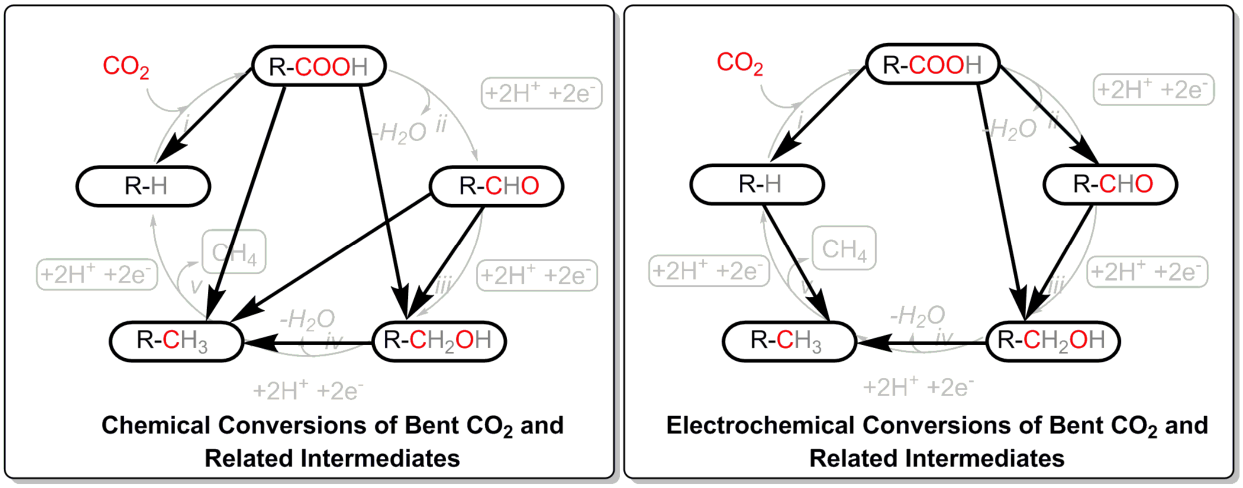
We survey the organic chemistry involved in the reduction of CO_2 and related intermediates to chemical fuels.

We describe chemical reactions of CO_2 with organic molecules to yield carboxylic acid derivatives that can get further reduced.

We point out reactions such as the Cross Canizzaro and the Eschweiler Clark as possible non-faradaic chemical reactions contributing to observed product distributions in the production of solar fuels from CO_2.


CO2
R-COOH
R-H
R-CHO
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i
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Chemical Conversions of Bent CO2 and Related Intermediates
Electrochemical Conversions of Bent CO2 and Related Intermediates